



Novel proton exchange membranes based on cardo poly(arylene ether sulfone/nitrile)s with perfluoroalkyl sulfonic acid moieties for passive direct methanol fuel cells

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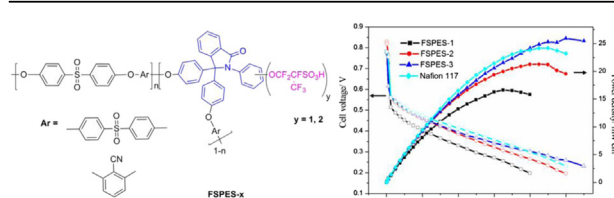
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HIGHLIGHTS

- FSPES-*x* membranes with perfluoroalkyl sulfonic acid groups were synthesized.
- The perfluorosulfonated reaction without employing any metal and basic catalysts.
- FSPES-3 shows high conductivity, OCV and superior cell performance.

GRAPHICAL ABSTRACT



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ABSTRACT

A new series of cardo poly(arylene ether sulfone/nitrile)s FSPES-*x* with perfluoroalkyl sulfonic acid groups have been successfully prepared by the perfluorosulfonic acid lactone ring-opening reaction without using any metal or base catalysts. These materials have been characterized by IR, NMR and TGA. The results indicate that this simple and metal-free method of preparation is highly efficient for controlling both the degree of perfluorosulfonation and the position of the sulfonate group and no side reactions such as crosslinking is observed. The FSPES-*x* membranes ($\text{IEC} = 1.17\text{--}1.64 \text{ m equiv g}^{-1}$) show the desired characteristics such as good film-forming ability, excellent thermal and mechanical properties, low methanol permeability, high conductivity (up to 0.083 S cm^{-1} at room temperature), as well as appropriate cell performance compared to Nafion[®]117. With these properties, such fluorinated sulfonic acid side-chain-type polymers are promising PEM materials for application in fuel cells.

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1. Introduction

The proton exchange membranes (PEMs) are key components of direct methanol fuel cells (DMFCs) which are of great interest in both academia and industry due to their potential for a wide range

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of applications, especially in the area of portable power generation [1,2]. Over the past decade, significant research efforts have been devoted to the design of membrane materials with the intention of meeting the following requirements: high proton conductivity, low methanol permeability, high chemical and mechanical stability and low cost [3–5]. Numerous PEMs have been designed and studied with varying degrees of success, including perfluorosulfonic acid polymers and aromatic hydrocarbon polymers [6–9]. Recently, aromatic polymers containing perfluorosulfonic acid groups as new PEMs have attracted increasing attention since they combine the advantages of perfluorosulfonic acid polymers (excellent proton

conductivity, good mechanical and chemical stability) and aromatic hydrocarbon polymers (diverse structures and low cost) [10–19]. On the one hand, the presence of electron-withdrawing F atoms in their structures significantly increases the acid strength of the terminal sulfonic acid groups which effectively improves the proton concentration and proton mobility, thereby enhancing the proton conductivity. The high contrast in the polarity between the aromatic backbone architecture and the side chain of the polymer can facilitate phase separation between the hydrophilic and hydrophobic aggregates forming interconnected nano-channels for efficient proton-transport. Pioneering work on perfluorosulfonated aromatic polymers have been carried out by Watanabe and co-workers [10]. They have shown that perfluorosulfonated aromatic polymers possess many desirable properties such as good thermo- and chemical stability, high proton conductivity, and excellent mechanical performance.

A number of different approaches have been utilized for the development of perfluorosulfonated aromatic polymers which include the Ullmann reaction [10–15], Suzuki coupling (using transition metal catalyst) [16], and nucleophilic substitution (using basic catalyst) [17,18]. For the Ullmann reaction, the instability of the polymer containing bromo or iodo groups restricts the choice of subsequent reactions and the reaction conditions (long time, high temperature) are harsh with the conversion yield being low. Most importantly, the degree of perfluorosulfonation cannot be precisely controlled [10,11]. For nucleophilic substitution, the phenylenediamine or bisphenol monomers containing perfluorosulfonic acid groups are relatively scarce and the synthesis methods are complicated [17,19]. Therefore, exploring simple and environment-friendly, especially metal-free methods for the preparation of perfluorosulfonated aromatic polymers by precisely controlling the degree of perfluorosulfonation remains a challenge.

Our previous work indicated that easily obtained cardo poly(ether sulfone)s containing an active reaction site acts as a good building block for the construction of sulfonated aromatic polymers [20–22]. Therefore, we have used it to prepare the new type of cardo poly(arylene ether sulfone/nitrile)s with perfluoroalkyl sulfonic acid groups via the lactone ring-opening reaction. Compared to the Ullmann reaction and nucleophilic substitution, this method allows the precise control of the degree of perfluorosulfonation without the application of metal or basic catalysts due to the high reactivity of the perfluorosulfonic acid lactone and the hydroxyl group. The new type of cardo poly(arylene ether sulfone/nitrile)s FSPES-*x* synthesized, with perfluoroalkyl sulfonic acid groups display superior properties, such as lower water uptake and higher proton conductivities, in comparison with some reported sulfonated poly(arylene ether sulfone/ketone)s containing pendent sulfoalkyl groups [23,24] and sulfohenyl groups [25,26]. To the best of our knowledge, this is the first reported example of aromatic PEMs with pendent perfluoroalkyl sulfonic acid groups prepared via the lactone ring-opening reaction. In this work, we have described the preparation of new perfluorosulfonated aromatic polymers by combining their desirable properties including water uptake, proton conductivity, methanol permeability, chemical and mechanical stability, and cell performance.

2. Experimental section

2.1. Materials

1,2,2-Trifluoro-2-hydroxy-1-trifluoromethylethane-sulfonic acid sulfone, 2,6-difluorobenzonitrile, bis(4-fluorophenyl)sulfone and boron tribromide were obtained from Sigma–Aldrich and used as received. Phenolphthalein (PPH) was purchased from the Beijing Chemical Reagent Company. 4-methoxyaniline and 3,5-dimetho-

xaniline were obtained from TCI and used as received. Dimethyl sulfoxide (DMSO) was dried with CaH₂ and distilled under reduced pressure before use. All other chemicals were reagent grade and used as received.

2.2. Synthesis of monomer **1a**

A 500 mL, three-necked, round-bottom flask equipped with a mechanical stirrer, gas inlet and condenser was charged with 10.0 g (0.031 mol) of PPH, 11.97 g (0.075 mol) of 4-methoxybenzenamine chloride and 21.55 g (0.175 mol) of 4-methoxyaniline. This solution was heated at 200 °C for 8 h. After this the solution was poured into deionized water, and the white precipitate obtained was filtered to give the crude product which was recrystallized from a mixture of ethanol and water. Yield: 75%.

¹H NMR (300 MHz, DMSO; ppm): δ 9.54 (s, 2H), 7.80 (d, *J* = 6.0 Hz, 1H), 7.60 (t, 1H), 7.50 (t, 1H), 7.22 (d, *J* = 9.0 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 4H), 6.77 (d, *J* = 6.0 Hz, 4H), 6.66 (d, *J* = 9.0 Hz, 4H), 3.68 (s, 3H); ES-MS: 424.2 (M + H)⁺

Monomer **1b** was prepared by following the same method as described above. Yield: 70%.

¹H NMR (300 MHz, DMSO; ppm): δ 9.57 (s, 2H), 7.81 (d, *J* = 6.0 Hz, 1H), 7.60 (t, 1H), 7.50 (t, 1H), 7.25 (d, *J* = 9.0 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 4H), 6.67 (d, *J* = 6.0 Hz, 4H), 6.32 (s, 1H), 6.11 (s, 2H), 3.55 (s, 3H); ES-MS: 454.2 (M + H)⁺

2.3. Typical synthetic procedures for the synthesis of PES-*x*

A typical synthetic procedure for PES-1 is described as follows: compound **1a** (2.12 g, 5.0 mmol), bis(4-fluorophenyl)sulfone (1.27 g, 5.0 mmol), K₂CO₃ (897 mg, 6.5 mmol) and DMSO (20 mL) were added into a 50 mL three-necked flask equipped with a mechanical stirrer and a nitrogen inlet. The reaction mixture was kept at 140 °C for 4 h to give a viscous solution. After 4 h, the solution was poured into 500 mL of deionized water with vigorous stirring. The resulting solid product was washed with deionized water and hot methanol several times and dried at 80 °C under vacuum for 24 h. Yield: 98%.

PES-2, 3 were prepared by following the same method as described above. Yield >90%.

2.4. Typical synthetic procedures for the synthesis of FSPES-1

For the synthesis of FSPES-1 the copolymer PES-1-OH was synthesized first by following the procedure as described herein. A sample of 2.0 g of PES-1 was dissolved in 50 mL of CHCl₃ in a 100 mL three-necked flask equipped with a mechanical stirrer and a nitrogen inlet. BBr₃ (2 mL) was diluted with CHCl₃ (20 mL), and the resulting solution was added dropwise to the PES-1 solution at 0 °C, whereby the reaction temperature gradually reached room temperature. After 12 h, the resulting copolymer (PES-1-OH) was filtered, washed with boiling water, and then dried under vacuum at 100 °C for 24 h. Yield: 90%.

Samples of 1.5 g of PES-1-OH were dissolved in 30 mL of DMSO at room temperature and stirred for 20 min under nitrogen atmosphere, after which 1.6 g of 1,2,2-Trifluoro-2-hydroxy-1-trifluoromethylethane-sulfonic acid was added to it. The mixture was further stirred for 30 min and then heated to 110 °C for another 12 h. The viscous solution was poured into 500 mL of water and the precipitate thus obtained was washed with boiling water several times before being dried under vacuum at 100 °C for 24 h. Yield: 95%.

FSPES-2, 3 was prepared by following the same method as described above. Total yield: > 80%.

2.5. Membrane preparation

The sulfonated copolymers were cast onto a glass plate from their DMAc solution (5–8 weight %) after filtration. The removal of DMAc was accomplished in an oven at 60 °C for 8 h and then at 120 °C under vacuum for 10 h. The polymer membranes were treated with 1.0 N sulfuric acid at room temperature for 2 days, followed by thoroughly washed with deionized water and then dried under vacuum at 100 °C for 10 h. Tough and ductile ionomer membranes were obtained with a controlled thickness of 40–60 μm.

2.6. Measurements

¹H NMR spectra were measured at 300 MHz on an AV 300 spectrometer. Thermogravimetric analysis (TGA) was performed in air atmosphere on a TA Instrument TGA Q500 thermogravimetric analyzer from 50 to 800 °C with the heating rate of 10 °C min⁻¹. Tensile measurements were conducted with an Instron-1211 at a speed of 1 mm min⁻¹ at room temperature and ambient humidity conditions. The size of samples was 20 × 5 mm. For TEM observations, the membranes were stained with lead ions by ion exchange of the sulfonic acid groups in 1 wt% Pb(OAc)₂ aqueous solution for 2 days, rinsed with deionized water and then dried at room temperature for 2 days.

The water uptake and swelling ratio were determined by measuring the difference in weight and length between dry and hydrated membranes.

Water uptake of the membranes was calculated from the equation (1):

$$\text{Water uptake(\%)} = [(W_w - W_d)/W_d] \times 100 \quad (1)$$

where W_d and W_w are the weights of dry and corresponding water-swollen membranes, respectively.

The water swelling ratio of the polymer membranes was calculated from the equation (2):

$$\text{Swelling ratio(\%)} = [(l_w - l_d)/l_d] \times 100 \quad (2)$$

where l_d and l_w are the diameters of dry and wet membranes, respectively.

The oxidative stability of SPES-x membranes was evaluated by changes in molecular weight of membranes after they were soaked in Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C for 1 h.

The proton conductivity (σ, S cm⁻¹) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $s = d/LsWsR$ (d is the distance between the adjacent electrodes, and Ls and Ws are the thickness and width of the membrane, respectively). The resistance value (R) was measured over the frequency range of 100 mHz–100 KHz by four-point probe AC impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the adjacent electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in deionized water for measurement. At a given temperature, the samples were equilibrated for at least 30 min before measurements. Repeated measurements were taken at the desired temperature with 10-min interval until no more changes in conductivity were observed.

The methanol permeability was determined by using a cell consisting of two half-cells separated by the membrane, which was fixed between two rubber rings. Methanol (2 mol L⁻¹) was placed

on one side of the diffusion cell, and deionized water was placed on the other side. Magnetic stirrers were used in each compartment to ensure uniformity. The concentration of methanol was measured by a SHIMADZU GC-1020A series gas chromatograph. Peak areas were converted into methanol concentration with a calibration curve. The methanol permeability was calculated by the equation (3):

$$C_B(t) = \frac{A}{V_B} \cdot \frac{DK}{L} \cdot C_A \cdot (t - t_0) \quad (3)$$

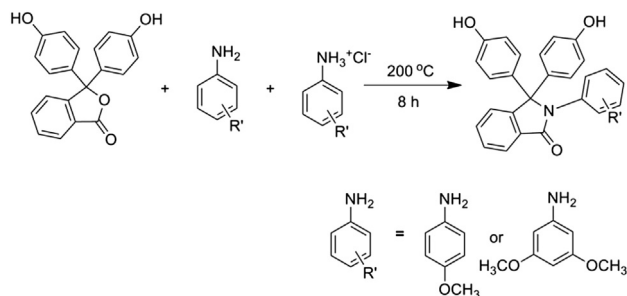
where C_A and C_B are the methanol concentration in the field and in permeate, respectively. A , L and V_B are the effective area, the thickness of the membrane and the volume of permeated compartment, respectively. DK is defined as the methanol permeability and t_0 is the time lag.

The membrane electrode assembly (MEA) with FSPES-x and Nafion®117 membranes was made according to the literature method [27]. A slurry which consisted of Vulcan XC-72 carbon and PTFE (20 wt.%) was coated onto the carbon paper (TGPH060, 20 wt.% PTFE, Toray) to form the cathodic microporous layer (MPL). The XC-72 carbon loading was ca.2 mg cm⁻². For the preparation of anodic MPL, a slurry consisting of carbon materials and PTFE (20 wt.%) was coated onto the carbon paper (TGPH060, 0 wt.% PTFE, Toray) to form the anodic MPL. The total carbon loading was ca. 1 mg cm⁻². The anode and cathode catalysts used in this work were Pt–Ru black with an atomic ratio 1:1 (HiSpec 6000, Johnson Matthey) and carbon-supported Pt with a Pt loading of 60 wt.% (HiSpec 9000, Johnson Matthey), respectively. Catalyst ink was prepared by dispersing appropriate amount of catalyst and 5 wt.% Nafion solution (Aldrich) into a mixture of isopropyl alcohol and ultrapure water with a volume ratio of 1:1. The catalyst ink was then sprayed on the MPL. The metal loading was 4.0 ± 0.2 mg cm⁻² for both cathode and anode, and the ionomer loading was 20 wt.% for the cathode and 15 wt.% for the anode, respectively. The membrane electrode assemblies were prepared by hot-pressing both anode and cathode on both sides of Nafion®117 and FSPES-x membrane at 6 MPa for 3 min at 130 °C and 150 °C, respectively. The polarization curves of the passive DMFCs at room temperature were obtained on an Arbin FCT testing system (Arbin Instrument Inc. USA) by using 4 M methanol aqueous solution as fuel. At each discharging current point along the polarization curve, a 2 min waiting period was kept to obtain a stable voltage reading.

3. Results and discussion

3.1. Synthesis and characterization of monomers

Two novel bisphenol monomers **1a** and **1b** with methoxy functionality were readily prepared from phenolphthalein and 4-methoxyaniline or 3,5-dimethoxyaniline in one step according to the known reaction sequences [20]. Scheme 1 shows the synthetic



Scheme 1. The synthetic route for bisphenol monomers **1a** and **1b**.

route for the monomers **1a** and **1b**. Running the reaction for 8 h at 200 °C followed by recrystallization generally resulted in yields of approximately 75% for **1a** and 70% for **1b** (based on phenolphthalein). Their structures were confirmed from ^1H NMR spectra (Fig. 1). The peaks at 3.6 ppm and 9.6 ppm can be assigned to the hydrogen atoms of methoxy group and the phenolic hydroxyl group, respectively. The location and integral area of other peaks were consistent with those of the desired compounds which indicated that the methoxy-substituted bisphenol monomers **1a** and **1b** were successfully synthesized.

3.2. Synthesis and characterization of copolymer

The novel cardo poly(arylene ether sulfone/nitrile) copolymers PES-1 and 2 were first synthesized by the copolymerization of new bisphenol monomer **1a** and bis(4-fluorophenyl) sulfone or 2,6-difluorobenzonitrile under nucleophilic aromatic substitution conditions (Scheme 2). These copolymers were then de-protected with boron tribromide in CHCl_3 at room temperature and the desired PES-*x*-OH was obtained in good yield. The generation of this hydroxyl group after deprotection creates a reactive site for further functionalization. This PES-*x*-OH copolymer reacted with the highly active perfluoroalkyl sulfonic acid lactone through the ring-opening reaction (without base under 110 °C) to provide new cardo (arylene ether sulfone/nitrile)s FSPES-1 and 2 with the perfluoroalkyl sulfonic acid groups as shown in Scheme 2.

The chemical structures of the synthesized copolymers were characterized by ^1H NMR spectroscopy with $\text{DMSO}-d_6$ as the solvent. Fig. 2 shows ^1H NMR spectra of PES-1, PES-1-OH and FSPES-1. The complete disappearance of the peak due to the methoxy group at 3.6 ppm and the appearance of a new peak at 9.54 ppm confirmed the complete conversion or deprotection of the methoxy group to the phenolic hydroxyl group. In addition, there were remarkable changes in the ^1H NMR spectrum of FSPES-1 compared to that of PES-1-OH. The disappearance of the hydroxyl signal indicated that the perfluoroalkyl sulfonic acid groups were completely grafted onto SPES-*x*-OH. The peak area integration was also consistent with the expected structure of FSPES-1.

The structure of FSPES-*x* was also analyzed by ^{19}F NMR to examine the change in molecular structure. For example, as shown in Fig. 3, the three ^{19}F signals at −130, −118 and −65 ppm have isotropic chemical shifts that are consistent with the relative stoichiometries (1:2:3) of the $-\text{CF}$, $-\text{CF}_2$, and $-\text{CF}_3$ fluorine moieties respectively, of the grafted perfluorosulfonic acid species, suggesting that the desired product FSPES-1 was successfully obtained.

The chemical structure of the polymers was also confirmed by FT-IR spectra. In the fingerprint area of each spectrum, a strong band was found at 1240 cm^{-1} , representing the C–O stretching of

the ether linkage. As shown in the FT-IR spectra (Fig. 4), PES-1-OH shows a new characteristic band at 1034 cm^{-1} that can be assigned to the stretching vibration of the phenolic hydroxyl group. When compared to the spectra of PES-1, this indicates the conversion of the ether bond to the phenolic hydroxyl group. FSPES-1 shows the characteristic band at 1207 cm^{-1} as compared to unsulfonated PES-1 and PES-1-OH which can be assigned to the $\text{O}=\text{S}=\text{O}$ stretching vibration of the sulfonic acid groups. This indicates the successful introduction of perfluoroalkyl sulfonic acid groups into the polymers. In addition, the stretching vibrations of the carbonyl group in the phenolphthalein moiety are different in all the three polymers, 1702 cm^{-1} for FPES-1, 1678 cm^{-1} for FPES-1-OH, 1696 cm^{-1} for FSPES-1, which indicates changes in the substituted amide group. The resulting spectrum also confirms the successful introduction of perfluoroalkyl sulfonic acid groups to the FSPES-1 with a 100% degree of substitution.

In order to obtain random copolymers with densely localized concentrations of sulfonated units, another novel bisphenol monomer **1b** containing two methoxy groups in one benzene ring was designed. This novel bisphenol monomer can provide selective perfluorosulfonation sites which can achieve precise control of the content, quantity and density of sulfonic acid groups in the final copolymers. Finally, a densely localized sulfonated aromatic polymer FSPES-3 ($\text{IEC} = 1.64$) (shown in Fig. 5) was successfully prepared from bisphenol monomer **1b** under the same conditions.

Thus a new series of cardo poly(arylene ether sulfone/nitrile)s with perfluoroalkyl sulfonic acid groups have been successfully synthesized under mild conditions. This method avoids the use of metal catalysts such as copper or basic catalysts which are usually applied in the Ullmann reaction and nucleophilic substitution, respectively. Moreover, the degree of perfluorosulfonation and the site of substitution can be precisely controlled.

The IEC, viscosity and solubility values of the polymers are summarized in Table 1. The IEC values are close to the theoretical values, which indicate that the degree of sulfonation for the repeating unit is almost quantitative. The viscosities of FSPES-*x* between 0.83 and 1.28 dL g^{-1} indicates that large molecular weight cardo poly(arylene ether sulfone/nitrile)s with perfluoroalkyl sulfonic acid groups have been successfully prepared.

All the sulfonated polymers are soluble in polar solvents, such as DMSO, NMP, DMAc and DMF, but they are insoluble in ethanol and water. In addition, they exhibit good film forming and mechanical properties.

3.3. Thermal stability and mechanical properties

The thermal stabilities of the polymers were investigated by the TGA. The TGA curves of FSPES-*x* under nitrogen atmosphere

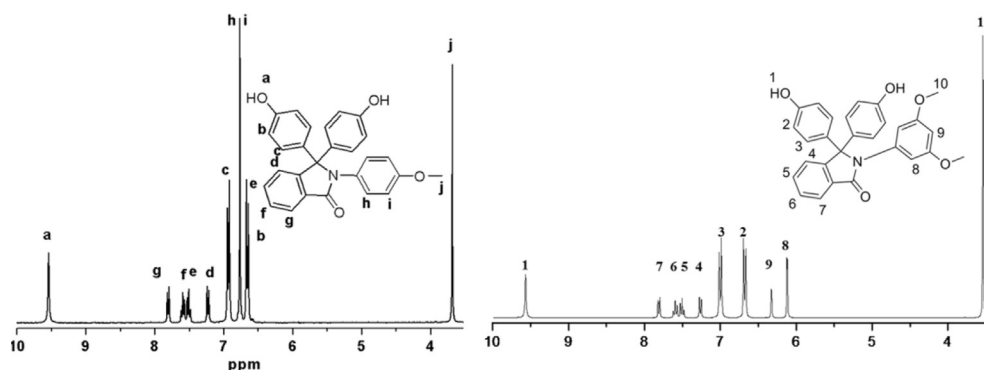
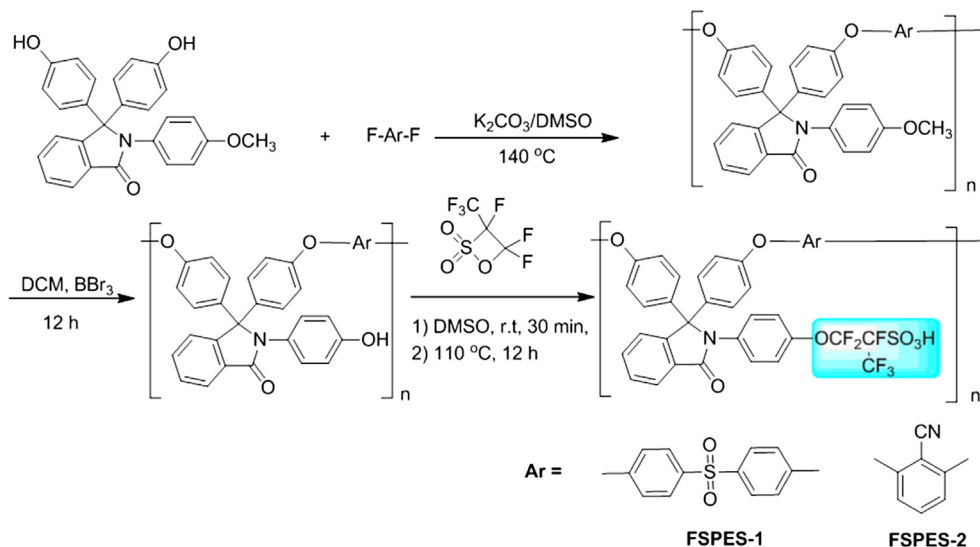


Fig. 1. ^1H NMR spectra of **1a** and **1b** in $\text{DMSO}-d_6$.



Scheme 2. The typical synthetic route for cardo poly(arylene ether sulfone/nitrile)s containing perfluoroalkyl sulfonic acid groups.

showed in Fig. 6 exhibit a typical two-step degradation pattern. The initial continuous degradation step observed from room temperature to ca. 450 °C, can be associated with the loss of water molecules absorbed by the highly hygroscopic $-\text{SO}_3\text{H}$ groups and thermal degradation of sulfonic acid groups. The second step observed from 450 °C can be attributed to the decomposition of the main polymer chains. The 5% weight loss temperature was above 300 °C, which is sufficiently high for fuel cell applications. Moreover, the first weight loss stage of FSPES-2 was delayed, which indicates that it has better thermal stability in the low temperature stage than others. This may be associated with strong hydrogen bonding interactions caused by the $-\text{CN}$ groups on the FSPES-2 backbone.

The mechanical properties of FSPES-*x* are summarized in Table 1. The SPES-*x* membranes show good mechanical properties with tensile modulus in the range of 29.4–38.8 MPa. These results indicate that with the increase in water uptake, the tensile strength of the FSPES-*x* membrane weakened resulting in an increase in elongation. This could be attributed to the plasticization effect of

water. This elasticity and flexibility of FSPES-*x* should improve its durability under fuel cell operation.

3.4. Water uptake, swelling ratio

Water uptake and swelling ratio have a profound effect on the proton conductivity and mechanical property of PEMs. For most proton conductive polymers, water plays an important role and acts as the carrier for proton transport through the polymer membrane [4,8]. Adequate hydration of electrolyte membranes is crucial for high proton conductivity. However, uptake of excess water in the membranes results in undesired dimensional change or loss of dimensional shape, which can lead to weakness or a dimensional mismatch when incorporated into a membrane electrode assembly (MEA) [4]. Thus an optimum water uptake is needed for dimensional stability and application for PEMs.

As shown in Fig. 7, the water uptake of FSPES-*x* follows approximately the order of their IECs and increases with the increase in temperature. Among the FSPES-*x* polymers, FSPES-3 showed the highest IEC value with its water uptake also being the highest. Even in the hydrated state at 80 °C, water uptake of the membrane was significantly low (only 34.1%). The comparatively low water uptake can be attributed to the rigid structure of the

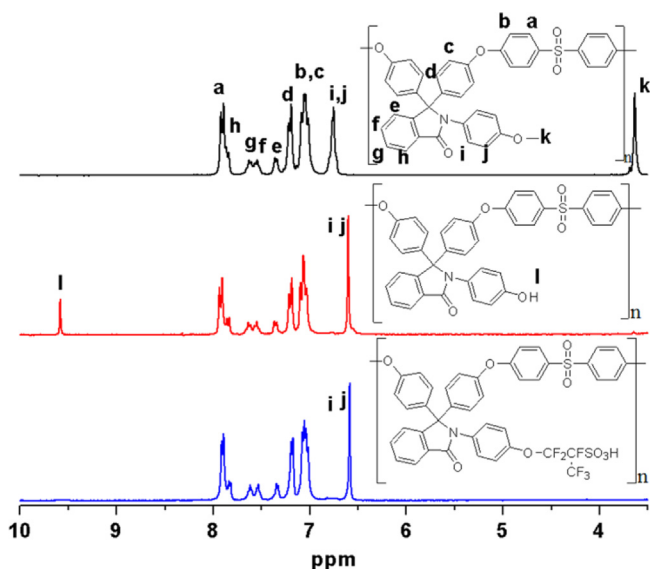


Fig. 2. ^1H NMR spectra of FSPES-1, FSPES-1-OH and FSPES-1 in $\text{DMSO}-d_6$.

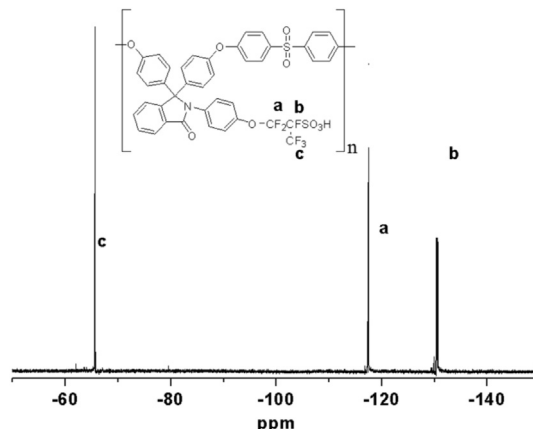


Fig. 3. ^{19}F NMR spectra of FSPES-1 in $\text{DMSO}-d_6$.

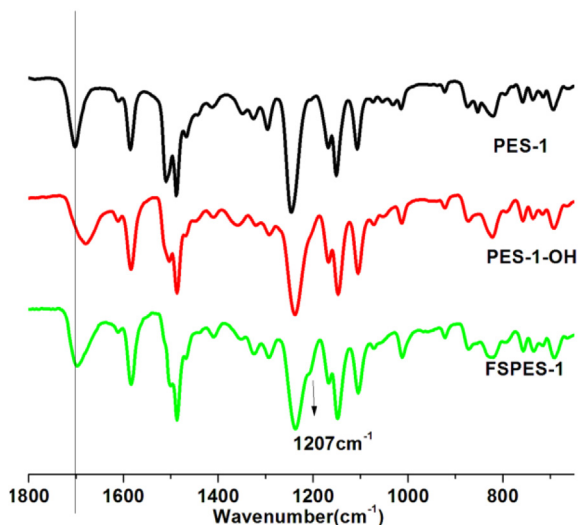


Fig. 4. FT-IR spectra of PES-1, PES-1-OH and FSPES-1.

main chain, short fluorinated side chain and high fluorine content. In addition, compared with the reported membranes with a similar IEC value but containing different sulfonate groups, FSPES-*x* membranes were found to absorb much less water than the aryl sulfonated membranes [22,25] and slightly more water than the alkyl sulfonates membranes [21,23]. This difference in the water uptake of the fluoroalkyl sulfonate sample compared to the alkyl sample can be attributed to the increased hydration of the superacid. Besides, FSPES-*x* membranes and superacidic fluoroalkyl sulfonates membranes have similar function of water uptake and temperature [16].

FSPES-*x* membranes demonstrated good dimensional stability and low swelling ratios within the tested temperature range, as shown in Table 1. The largest swelling ratio is about 16.3% at 80 °C, which is lower than that of Nafion® 117 (23.7%). FSPES-1 (IEC = 1.17 m equiv g⁻¹) exhibits relatively low water uptake (21.7%) and excellent resistance to hot water since the swelling ratio (in-plane direction) is only 10.1% at 80 °C. It indicates that the introduction of perfluoroalkyl sulfonic acid groups to the backbone of FSPES-*x* further improves the hydrophobic character of the polymer and effectively suppresses the swelling behavior. Moreover, the sterically bulky structure of the FSPES-*x* main chain can generate more free volume to incorporate water molecules [22,28]. These properties are obviously different from many reported sulfonated random polymers with similar IECs which always display an extraordinary increase in dimensional change especially at elevated temperatures [23–26].

3.5. Proton conductivity, methanol permeation and oxidative stability

Proton conductivity is a critical property of proton exchange membranes. The proton conductivities of the FSPES-*x* as well as

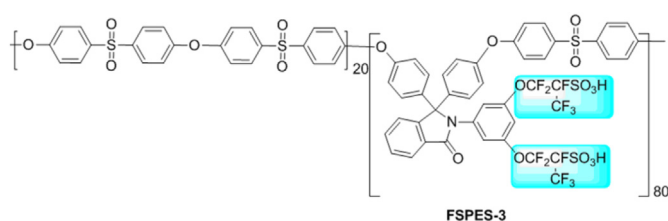


Fig. 5. Sulfonated cardo poly(arylene ether sulfone)s (FSPES-3).

Table 1
Some properties of FSPES-*x*.

Sample	IEC (m equiv g ⁻¹)		η^c (dL g ⁻¹)	TS ^d (MPa)	Swelling ratio (%)	
	Theo ^a	Exper ^b			20 °C	80 °C
FSPES-1	1.17	1.04	1.28	38.8	7.3	10.1
FSPES-2	1.35	1.30	1.17	35.1	8.8	14.2
FSPES-3	1.64	1.57	0.83	29.4	10.1	16.3

^a Calculated by ¹H NMR.

^b Measured by titration.

^c Intrinsic viscosities measured at a concentration of 0.5 g dL⁻¹ in NMP at 30 °C.

^d Samples were dried at ambient conditions for one day and tested at 30 °C, and ambient humidity conditions.

Nafion® 117 were measured in water within the temperature range of 30–80 °C. As shown in Fig. 8, the obtained FSPES-*x* copolymers exhibited high proton conductivities which increased with increasing temperature. The proton conductivity gradually decreased from FSPES-3 to FSPES-1, which can be attributed to the decrease in their IEC values. Among them, FSPES-3 showed the highest proton conductivity which is almost comparable with that of Nafion® 117 within the temperature range examined. Also, FSPES-3 gave comparable conductivity (0.083 S cm⁻¹) to PAE-BP (0.089 S cm⁻¹) even though the IEC of PAE-BP is 25% greater than that of FSPES-3 [18]. These results reveal that the introduction of perfluoroalkyl sulfonic acid groups into the aromatic polymer backbone effectively improves proton conductivity in comparison to some reported sulfonated poly (arylene ether sulfone)s containing pendent sulfoalkyl and sulfophenyl groups with the same IEC values [20,21,23–26]. This can be attributed to the strong acidity of perfluoroalkyl sulfonic acid groups which makes more protons free for conduction. Moreover, the pendent perfluoroalkyl sulfonic acid groups favor the separation of phases which is particularly important for PEM materials because it affects the water uptake and the proton transport pathway in the PEM [12,14,15].

A typical TEM image is shown in Fig. 9, in which the dark regions represent localized ionic domains and the light regions represent the hydrophobic polymer backbones. The TEM image shows that the sulfonic acid groups might aggregate into hydrophilic clusters thereby creating proton transport channels. This indicates that the introduction of perfluoroalkyl sulfonic acid groups is effective in improving the ionic channels and their interconnectivity, which are related to structural factors like hydrophobicity and flexibility of

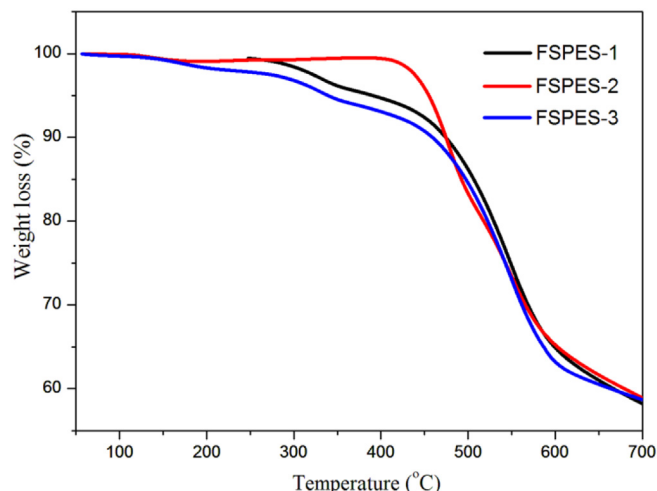


Fig. 6. TGA curves of FSPES-*x* under nitrogen atmosphere.

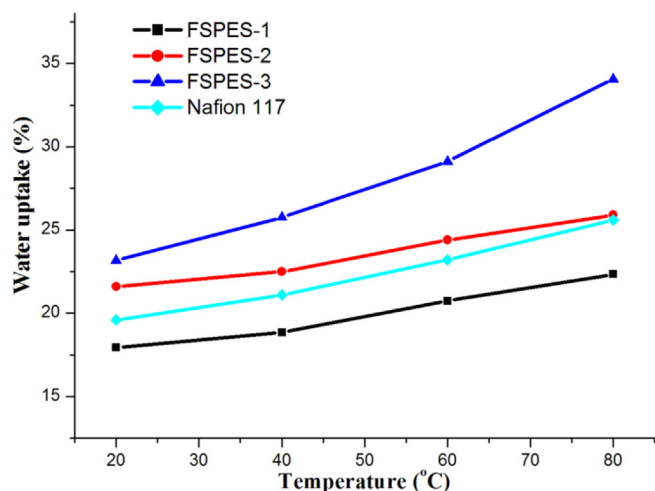


Fig. 7. The temperature dependence of water uptake of the sulfonated polymers and Nafion®117.

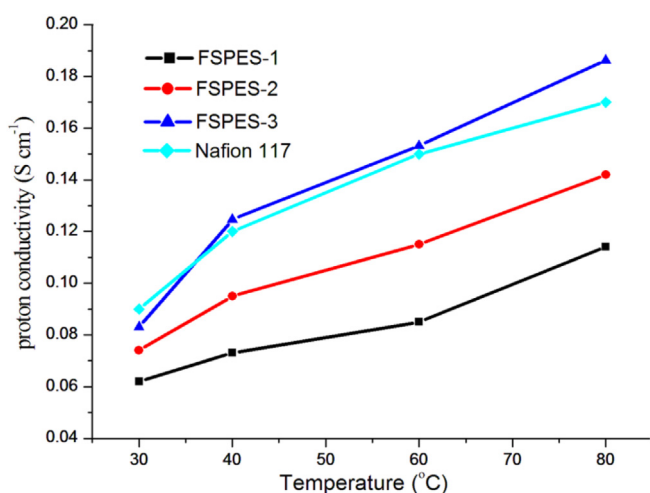


Fig. 8. The temperature dependence of proton conductivity of the sulfonated polymers and Nafion®117.

the side chains. This result is also in accordance with our previous observation regarding random copolymers, in which a pendent sulfonated aliphatic side chain moiety induced greater phase separation than main-chain-type ones [20].

Table 2

Proton conductivity and methanol permeability of sulfonated polymer membranes.

Sample	σ (S cm ⁻¹) ^a	P_M (cm ² S ⁻¹) 10 ⁻⁶	Selectivity (S s cm ⁻³) 10 ⁴	Oxidative stability ^b (wt %)
FSPES-1	0.062	0.77	8.05	95.4
FSPES-2	0.074	0.80	9.30	98.2
FSPES-3	0.083	0.90	9.22	90.9
Nafion®117	0.090	2.40	3.75	99.0

^a Measured under 100% RH environment at 30 °C.

^b Residue after treatment with Fenton's reagent (3% H₂O₂ aqueous solution containing 2 ppm FeSO₄) at 80 °C for 1 h.

Methanol permeation is a key parameter for direct methanol fuel cells (DMFCs) because high methanol permeation will decrease the efficiency of the fuel cell. As summarized in Table 2, the FSPES-*x* membranes exhibit low methanol permeability at room temperature, with values in the range of 0.77×10^{-6} to 0.90×10^{-6} cm² S⁻¹, which is lower than the value of 2.4×10^{-6} cm² S⁻¹ for Nafion®117. The selectivity, which is the ratio of proton conductivity (σ) to methanol permeability (P), is often used to estimate the membrane performance. That is to say, the higher the value of σ/P , the better the performance of the membrane would be. As listed in Table 2, the relative selectivity of FSPES-*x* is higher than that of Nafion®117 with FSPES-2 showing the highest selectivity. This can be attributed to the introduction of cyano groups which creates strong interactions or hydrogen bonds with other polar groups that brings the molecular chains more close, thereby preventing methanol permeation [29].

As a simulated accelerated test, the oxidative stability of the FSPES-*x* was investigated by immersing the membranes (the size of each sheet: 0.5×1.0 cm²) into Fenton's reagent (2 ppm FeSO₄ in 3% H₂O₂) at 80 °C. The data presented in Table 2 shows that after treating in Fenton's Reagent for 1 h, there were no changes in the appearance of these polymers and the weights remaining for all the FSPES-*x* samples were above 90.9%. Although the FSPES-3 membranes with high IEC values showed relatively low oxidative stability under Fenton's test conditions due to its higher water uptake and subsequent swelling, this drawback could be compensated by its low methanol permeability and high relative selectivity for its application in fuel cells.

3.6. Single-cell performance

Nafion®117 and FSPES-*x* membranes were tested in a passive DMFC single cell. Fig. 10 shows the performance results for them at room temperature, including the polarization and power density as

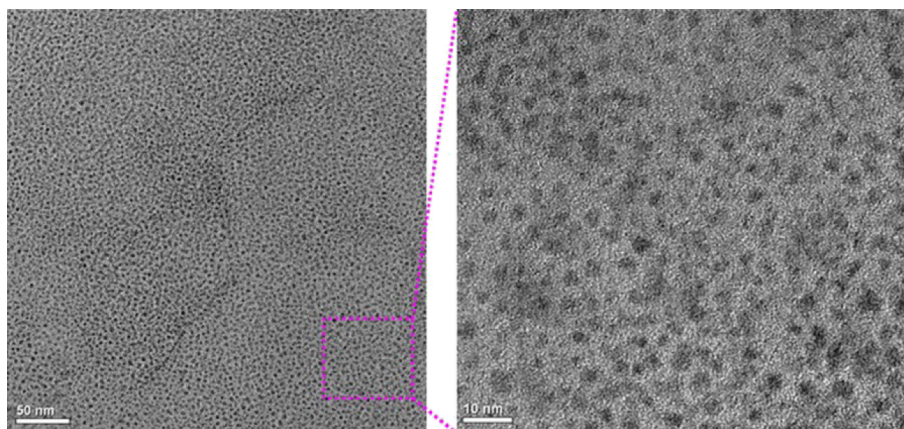


Fig. 9. TEM image of FSPES-3.

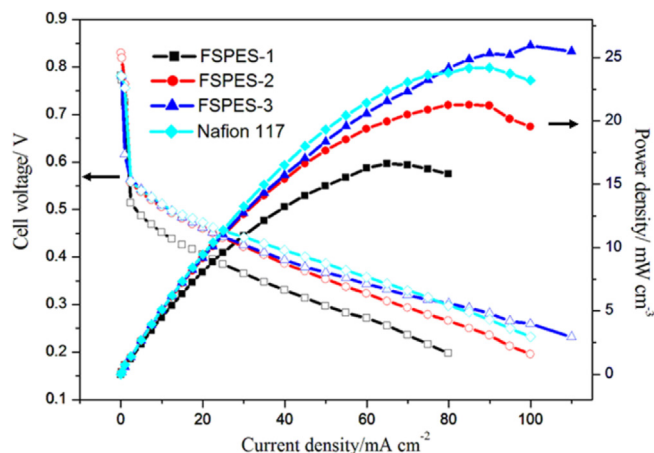


Fig. 10. Cell voltage/power density vs load current–density for passive DMFC with Nafion® 117 and FSPES-*x* membranes.

a function of the current density. All the characteristic curves displayed similar polarization behavior. It is well known that apart from activation control and intrinsic ohmic resistance that can contribute to a lower output upon application of a load to a system, methanol crossover also actively decreases the open circuit voltage (OCV). OCV is closely related to methanol permeation and it increases when the methanol crossover decreases [30]. Single cells prepared with the polymer membranes exhibited high OCVs of 0.79, 0.83, and 0.78 V for 4 M methanol at room temperature for FSPES-1, FSPES-2, and FSPES-3 respectively. These values are consistent with methanol permeability results and close to that of the conventional reference Nafion®117 (0.78 V). The higher OCV clearly indicates that FSPES-*x* membranes can significantly decrease the rate of methanol crossover in passive DMFCs. Therefore, even though the conductivity of FSPES-*x* membranes is lower than that of Nafion®117, the passive DMFC performance is better due to reduced methanol crossover. Among the FSPES-*x* membranes, FSPES-3 exhibits the highest power density of 25.9 mW cm⁻², which is higher than that of Nafion®117 (24.3 mW cm⁻²). This can be attributed to the much higher selectivity factor (σ/P) as compared with that of Nafion®117 (Table 2), and more densely localized concentrations of sulfonated units as compared with other FSPES-*x* membranes. These results indicate that the FSPES-*x* membranes with perfluoroalkyl sulfonic acid groups are promising materials for application in DMFCs.

4. Conclusions

In summary, we have developed a simple, general and efficient metal-free method for the synthesis of cardo poly(arylene ether sulfone/nitrile)s with perfluoroalkyl sulfonic acid groups. Most importantly, this simple method allows the precise control of the degree of perfluorosulfonation, owing to the high reactivity of the perfluorosulfonic acid lactone and the hydroxyl group. This results in a decrease in the reaction temperature and time and avoids using

metal and basic catalysts during the synthesis procedure. The experimental results reveal that FSPES-3 membrane with two perfluoroalkyl sulfonic acid moieties per polymer repeat unit exhibited high conductivity, OCV and superior single-cell performance compared with other FSPES-*x* membranes and Nafion®117. In addition, further studies which would be communicated in due course indicate that this facile method of synthesis can also be used for the substitution of aliphatic hydroxyl group, apart from the phenolic hydroxyl group reported herein.

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